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**Water Rock Interaction [WRI 14]**

# Uptake and retardation of Cl during cement carbonation

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**Abstract**

The presence of $^{36}Cl$ in low- and intermediate-level radioactive waste (L/ILW) is of concern in repository performance assessment. Its mobility and its relatively long half-life (302,000 years) could potentially lead to early release from the waste and its return to the biosphere within the $10^6$ timescale. Experiments have been undertaken to examine the impact of carbonation on the mineralogical and physical properties of NRVB cement in relation to the degradation of organic material in the L/ILW, and with oilwell Type-G cement in relation to borehole sealing for carbon capture and storage. These show that the cements can uptake a significant amount of Cl through the formation of transient secondary calcium chloroaluminate and Cl-rich calcium silicate hydrate phases. The formation of the Cl-rich phases is enhanced by carbonation reactions and also by low temperatures (20 °C). The process may be important in retarding the migration of $^{36}Cl$ from a repository for L/ILW.



Keywords: Chlorine retardation, cement carbonation; NRVB; oilwell cement, carbon dioxide,radioactive waste management

## 1. Introduction

Radionuclide mobility is a key issue in performance assessment (PA) of a geological disposal facility (GDF) for radioactive waste. The anionic radionuclides $^{36}Cl$, $^{129}I$, and $^{79}Se$ present as fission and activation products in spent fuel and low- and intermediate-level radioactive waste (L/ILW) [1], are of potential concern because of their relatively long half-lives (e.g. 302,000 years for $^{36}Cl$) and their high mobility [2]. Consequently, PA calculations take a conservative approach and suggest that these radionuclides will be leached from the repository, migrate through the far field, and enter the biosphere within $10^6$ years [2]. Therefore, the recognition of any processes that retard these mobile radionuclides will enhance and build confidence in a safety case for a GDF.

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The current UK repository concept for low and intermediate wastes involves using large quantities of cementitious materials for both construction and buffer/backfill. The potential alteration of cement by reaction with carbon dioxide ($CO_2$), from the degradation of organic material in the wastes, and its impact on the physical properties, has been investigated within the EC Framework 7 Fate of Repository Gases (FORGE) project. Experimental studies of $CO_2$-cement interaction have also been undertaken to evaluate the long-term stability of cement seals of injection wells in reservoirs and aquifers for geological storage of $CO_2$. Both of these experimental studies utilized saline pore fluids and show that significant interaction between chloride from the fluid and the cement matrix takes place during carbonation of the cement.

## 2. Methodology

Samples of Nirex Reference Vault Backfill (NRVB) cement were prepared as described by Francis et al. [3], cured at 40 °C for 28 days, and then stored in $Ca(OH)_2$-saturated water at room temperature. They were sub-cored to produce samples of 25 mm diameter x 50 mm long. The samples were reacted in batch reactors with a Na-Ca-OH-$SO_4$-Cl rich synthetic 'evolved' cement porewater (16,391 mg $l^{-1}$ $Cl^-$, initial pH 12.05 at 20 °C) under gaseous $CO_2$, 40 bar, 40 °C; liquid $CO_2$, 80 bar, 20 °C; supercritical $CO_2$ 80 bar, 40 °C; and under gaseous $N_2$ with the same range of conditions. The experimental system is described in detail in Rochelle and Sivers [4] and illustrated in Fig. 1.

A very similar experimental set up was used for the $CO_2$ storage cement interaction experiments (above), but experiments ran at 30 °C and 80 bar for 110 days [5]. The cement sample used was a low-permeability oil well Type G cement, and the starting fluid used was a Na-K-Ca-Cl porewater of approximately seawater composition (20,100 mg $l^{-1}$ $Cl^-$, initial pH 8.35 at 25 °C).

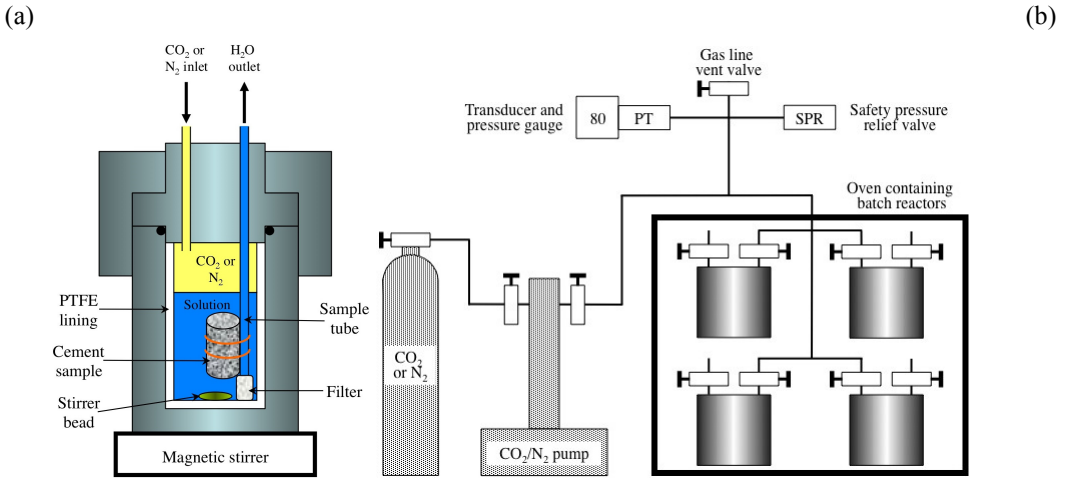


Fig. 1. (a) Schematic diagram of an assembled batch reactor. (b) Typical arrangement of batch reactors inside an oven.

The reacted cement cores were vacuum-dried at 20 °C. Polished thin sections were prepared (under ethanol) after impregnation with epoxy-resin. These were examined by optical petrographic microscope with detailed petrographic observations made by backscattered scanning electron microscopy (BSEM) supported by microchemical analysis by energy-dispersive X-ray microanalysis (EDXA). Digital element distribution maps were also recorded from selected areas of the sections using EDXA. Bulk mineralogical composition of the altered cement was determined by X-ray diffraction analysis (XRD).

## 3. Results

The experiments with NRVB and oil well Type G cement all showed a significant removal of $Cl^-$ from the porewater phase (e.g. Table 1). Reduction in $Cl^-$ was observed regardless of whether the porewater was in contact with gaseous $N_2$, or with gaseous, liquid or supercritical $CO_2$. $Cl^-$ removal was greater with $CO_2$ than with $N_2$, and increased with time. However, the reduction in $Cl^-$ concentration was considerably greater in the experiments at 20 °C with both gaseous $N_2$ (77% reduction in $Cl^-$) and liquid $CO_2$ (81% reduction in $Cl^-$), showing that temperature, rather than either the presence of $CO_2$ or $N_2$, or the phase of $CO_2$ had the greater controlling effect on $Cl^-$ uptake by the cement. This suggests that any secondary phases responsible for $Cl^-$ uptake in the cement are more stable at lower temperature.

Table 1. Chloride concentrations in the reacted fluid from batch experiments with NRVB cement under gaseous, liquid and supercritical $CO_2$ and gaseous $N_2$ environments.

| Experiment | Temp (°C) | Pressure (bar) | Time | Porewater Cl (mg $l^{-1}$) |
|---|---|---|---|---|
| Liquid $CO_2$ | 20 | 80 | 40 days | 3182 |
| Gaseous $CO_2$ | 40 | 40 | 40 days | 11325 |
| Supercritical $CO_2$ | 40 | 80 | 40 days | 12636 |
| Supercritical$CO_2$ | 40 | 80 | 1 year | 11205 |
| Gaseous $N_2$ | 20 | 80 | 40 days | 3773 |
| Gaseous $N_2$ | 40 | 40 | 40 days | 13074 |
| Gaseous $N_2$ | 40 | 80 | 40 days | 13408 |
| Gaseous $N_2$ | 40 | 80 | 1 year | 13007 |
| Starting porewater | | | | 16391 |

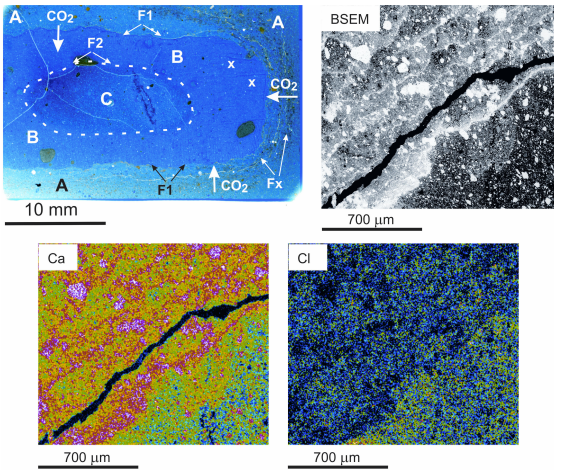


Fig. 2. Top left: Transmitted light photomicrograph of thin section through NRVB cement reacted for 40 days with FORGE evolved cement porewater and exposed to supercritical $CO_2$. A = fully-carbonated cement; B = partially carbonated cement; C = residual weakly carbonated cement core; F1 = main carbonation reaction front; F2 = diffuse inner reaction front; Fx = position of old reaction fronts; x = shrinkage cracks developed perpendicular to main carbonation front Top right: BSEM image detail of reaction front between fully carbonated cement zone (top) and partially carbonated cement. Bottom: EDXA distribution maps for Ca and Cl corresponding to same area as in BSEM image (colour scale: red = high concentration; black = low concentration).

The reacted cements in contact with gaseous $N_2$ exhibited little evidence of alteration. EDXA maps for Cl showed uniformly distributed low concentrations of Cl throughout the cement. However, cement from

experiments with $CO_2$ all showed significant carbonation alteration, with extensive replacement of the hydrated calcium silicates and aluminates by calcium carbonate (Fig. 2). Cement carbonation mainly occurred along a sharp front (Fig. 2), which progressively migrated from the edge to the centre of the cement cores. Carbonation was accompanied by volume reduction, with the development of shrinkage fractures parallel to, ahead and behind the carbonation front. EDXA mapping revealed that Cl was concentrated at, or just ahead of, the carbonation front in the cement. Detailed BSEM observations showed that fine-grained radial fibrous crystal aggregates of a calcium chloroaluminate phase and gel-like Cl-rich CSH had formed within or ahead of the carbonation front. XRD analysis of the altered cement indicates that the crystalline product is probably hydrocalumite ($Ca_4Al_2O_6Cl_2.10H_2O$). The Cl-rich phases are progressively dissolved and removed as the carbonation front moves forward, but reform on the cement side of the main reaction front. They are absent in the fully-carbonated cement zones.

## 4. Summary and conclusions

NRVB and oil well Type-G cement can both remove significant amounts of $Cl^-$ from porewater in contact with a non-reactive gas phase ($N_2$) or with gaseous, liquid or supercritical $CO_2$. However, $Cl^-$ removal is greatest during cement carbonation and at lower temperatures, implying that the formation of the secondary hydrocaluminite and Cl-rich CSH, responsible for incorporating $Cl^-$, is encouraged by reaction with $CO_2$ and stabilized by lower temperatures. However, the $Cl^-$ phase is metastable, and is progressively removed as the carbonation front moves through the cement. $Cl^-$ uptake by cement and formation of a Cl-rich secondary phase has been observed previously in experimental studies on cement carbonation and in oil well cement exposed to $CO_2$ for over 30 years [6][7]. The uptake of $Cl^-$ by the formation of transient secondary calcium chloroaluminate phases may provide an important mechanism for retarding the migration of $^{36}Cl$ from a GDF for radioactive waste.

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